Catalytic performance of Pt/ZrO_2 and $Pt/Ce\text{-}ZrO_2$ catalysts on CO_2 reforming of CH_4 coupled with steam reforming or under high pressure

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CO_2 reforming of methane was performed on Pt/ZrO_2 and $Pt/Ce\text{-}ZrO_2$ catalysts at 1073 K under different reactions conditions: (i) atmospheric pressure and $CH_4 : CO_2$ ratio of 1 : 1 and 2 : 1; (ii) in the presence of water and $CH_4 : CO_2$ ratio of 2 : 1; (iii) under pressure (105 and 190 psig) and $CH_4 : CO_2$ ratio of 2 : 1. The Pt supported on ceria-promoted ZrO_2 catalyst was more stable than the Pt/ZrO_2 catalyst under all reaction conditions. We ascribe this higher stability to the higher density of oxygen vacancies on the promoted support, which favors the cleaning mechanism of the metal particle. The increase of either the $CH_4 : CO_2$ ratio or total pressure causes a decrease in activity for both catalysts, because under either case the rate of methane decomposition becomes higher than the rate of oxygen transfer. The $Pt/Ce\text{-}ZrO_2$ catalyst was always more stable than the Pt/ZrO_2 catalyst, demonstrating the important role of the support on this reaction.

KEY WORDS: CO_2 reforming of methane; Pt/ZrO_2 and $Pt/Ce\text{-}ZrO_2$ catalysts.

1. Introduction

The CO_2 reforming of methane is a potential route to produce synthesis gas from natural gas. One advantage of dry reforming is that the synthesis gas produced has a H_2/CO ratio of 1 : 1, which is particularly attractive for the production of oxo-alcohols, polycarbonates, formaldehyde, acetic acid and pure CO [1]. Another positive aspect is the high CO purity that may be obtained [2]. Perhaps the most important advantage of dry reforming is the simultaneous availability of both reactants, CH_4 and CO_2. Some natural gas reservoirs have significant concentrations of CO_2, which minimize the cost of concentrating CO_2 [1].

In spite of these advantages, the major problem preventing commercialization of this process is the formation of coke, which deactivates the catalyst [1]. The problem of coke deposition can be overcome (i) by developing catalysts that minimize the rate of methane decomposition and/or CO disproportion [3]; (ii) by adding water or oxygen to the feed gas stream [4].

It has been demonstrated that the support plays an important role on the suppression of carbon formation on supported group VIII metals during CO_2 reforming of CH_4 [5–8]. Several studies have shown that Pt/ZrO_2 catalysts exhibit high activity and stability, even under severely deactivating conditions [9–14]. It has been proposed that the mechanism for the CO_2 reforming on Pt/ZrO_2 catalyst involves two independent paths [14–16]. Methane decomposition occurs on the metal, resulting in the formation of hydrogen and carbonaceous deposits. The carbon species react with lattice oxygen from the ZrO_2 near the metal particle to produce CO. The role of the support is to adsorb CO_2 at the oxygen vacancies and facilitate the dissociation at the metal–support interface.

Recently, we showed that the addition of promoters such as lanthanum and cerium improved catalyst activity and stability [17–19]. The addition of the lanthanum and cerium decreased the sintering of ZrO_2 during high-temperature calcinations, resulting in higher surface areas for the promoted catalysts. In addition, the addition of cerium lead to an increase in the oxygen vacancies necessary for CO_2 dissociation, which enhanced the cleaning capacity and catalyst stability. A correlation between support reducibility and catalytic activity was established, supporting the two-path mechanism.

Another strategy to decrease the coke formation is to couple CO_2 reforming with steam reforming [4,20]. Furthermore, the combination of these two reactions allows the control of the H_2/CO ratio through the variation of CO_2/H_2O ratio. Hegarty *et al.* [20] conducted CO_2 reforming of methane on a Pt/ZrO_2 catalyst in the presence of different water contents. In that study, it was observed that the water vapor addition caused an increase in both activity and H_2/CO ratio. However, the stability of the catalyst was not studied.

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The aim of the present work was to evaluate the activity and stability of Pt/ZrO$_2$ and Pt/Ce-ZrO$_2$ catalysts on CO$_2$ reforming coupled with steam reforming. In addition, the catalytic behavior of these catalysts for the dry reforming at high pressures was investigated. Temperature-programmed oxidation was used after reaction to study the nature of the coke deposits.

2. Experimental

2.1. Catalyst preparation

Zirconium hydroxide and the ceria-doped zirconia (18% CeO$_2$) used as supports were obtained from Magnesium Electron Inc. (MEI). The supports were calcined at 1073 K for 4 h in flowing air. The catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of H$_2$PtCl$_6 \cdot$ 6H$_2$O (Johnson Matthey). After impregnation and drying, the samples were calcined in air (30 cm^3/min) at 673 K for 2 h. The Pt/ZrO$_2$ and Pt/Ce-ZrO$_2$ catalysts had a Pt loading of 1.5 wt%.

2.2. Catalytic activity

The reactions at atmospheric pressure were performed in a quartz flow reactor at 1073 K. The samples (10 mg) were reduced under H$_2$ (30 cm^3/min) at 773 K for 1 h, and then heated to the reaction temperature in He (30 cm^3/min.). Ratios of CH$_4$: CO$_2$ that varied between 1 : 1 and 2 : 1 and a fixed total flow rate of 150 cm^3/min were used in each run. For the experiments of combined CO$_2$ and steam reforming, water was injected continuously through a syringe pump (SARGE instruments) at a flow rate of 15 cm^3/min. During the steam-reforming reaction, argon was added in the place of CO$_2$ in order to keep the same space velocity. The exit gases were analyzed on line by a Hewlett Packard GC equipped with a thermal conductivity detector and a Supelco Carboxen 1006 PLOT fused silica capillary column (30 m, 0.53 mm ID).

The high-pressure runs ($p = 105$–190 psig) were carried out in a stainless steel reactor (at 1073 K) with a back-pressure regulator valve (TESCOM). The samples (10 mg catalyst + 30 mg SiO$_2$) were pretreated under the same conditions as described above. The reaction feed contained a 2 : 1 ratio of CH$_4$: CO$_2$ and a total flow rate of 120 cm^3/min. The reaction products were analyzed on line by a Hewlett Packard GC equipped with a thermal conductivity detector and a Haysep C column. A common problem found in many papers reporting methane reforming results is that the data have been obtained under conditions in which equilibrium or mass and heat transfer limitations mask the real trends of activity and stability. All of the experiments obtained in this work were performed at low conversions and far from the equilibrium in order to minimize the mass and heat transfer limitations.

2.3. Temperature-programmed oxidation (TPO)

TPO experiments were carried out in a tubular cell coupled to a quadrupole mass spectrometer (MKS, PPT 4.24). The TPO analyses of carbonaceous deposits were used to determine the amount of carbon that was deposited under reaction conditions. These experiments were also used to provide information about the location of carbon. After reaction, the samples were cooled to room temperature in He, then heated at a rate of 8 K/min in a 5% O$_2$/He mixture (30 cm^3/min) up to 1073 K. After the system reached 1073 K, 100 μL of CO$_2$ pulses were injected in order to calculate the amount of coke formed on the catalysts under the various reaction conditions.

3. Results and discussion

The CH$_4$ and CO$_2$ conversions for the Pt/ZrO$_2$ and Pt/Ce-ZrO$_2$ catalysts for the CO$_2$ reforming reaction at atmospheric pressure under different conditions are summarized in table 1 and figures 1 to 3.

3.1. CO$_2$ reforming of methane

The conversions of CH$_4$ and CO$_2$ on the CO$_2$ reforming of methane using a CH$_4$: CO$_2$ ratio of 1 : 1 on Pt/ZrO$_2$ and Pt/Ce-ZrO$_2$ catalysts are shown in figure 1. The Pt/ZrO$_2$ catalyst exhibited a strong deactivation (figure 1(a)). After 22 h of reaction, the CH$_4$ and CO$_2$ conversions decreased from 37 and 43% to 22 and 29% respectively. By contrast, the Pt/Ce-ZrO$_2$ catalyst was very stable at any conversion level (figure 1(b)). In fact, the CH$_4$ and CO$_2$ final conversions were higher than the ones on the Pt/ZrO$_2$ catalyst. Hegarty et al. [20] only observed a small deactivation of the Pt/ZrO$_2$ catalyst on the CO$_2$ reforming of methane at 1073 K and CH$_4$: CO$_2$ ratio of 1 : 1. According to them, the deactivation was due to carbon deposition [9,20]. However, they used a larger amount of catalyst (50 mg) and the conversions were very near to the equilibrium conditions. The dry reforming reaction is very fast and involves a very high heat of reaction. Working close to the equilibrium at the oven temperature may be misleading since the temperature of the catalyst bed and more so inside the catalyst pores may be much lower than the set point of the temperature controller. Therefore, only data taken at low conversion can be safely used to compare catalyst stability.

Figure 2 displays the results of activity for the CO$_2$ reforming of methane on Pt/ZrO$_2$ (figure 2(a)) and Pt/Ce-ZrO$_2$ (figure 2(b)) catalysts under higher

Table 1
CH$_4$ and CO$_2$ conversions and H$_2$/CO ratio on the CO$_2$ reforming of methane under different reactions conditions

Catalyst	Total pressure (atm)	Feed	Methane reaction rate (gmol/g/min)			H$_2$/CO ratio		
			0	8	22	0	8	22
Pt/ZrO$_2$	1	CH$_4$/CO$_2$ (1:1)	0.1135	0.0859	0.0675	0.58	0.49	0.44
Pt/ZrO$_2$	1	CH$_4$/CO$_2$ (2:1)	0.1350	0.0614	0.0532	0.52	0.42	0.37
Pt/ZrO$_2$	1	CH$_4$/CO$_2$ (2:1)/H$_2$O	0.1718	0.0532	0.0409	0.93	0.82	0.45
Pt/ZrO$_2$	1	CH$_4$/H$_2$O	0.0573	0.0532	–	2.80	2.80	–
Pt/ZrO$_2$	8	CH$_4$/CO$_2$ (2:1)	0.6215	0.2290	–	0.49	0.44	–
Pt/ZrO$_2$	14	CH$_4$/CO$_2$ (2:1)	1.374	0.2863	–	0.61	0.37	–
Pt/Ce-ZrO$_2$	1	CH$_4$/CO$_2$ (1:1)	0.0920	0.0920	0.0951	0.41	0.41	0.41
Pt/Ce-ZrO$_2$	1	CH$_4$/CO$_2$ (2:1)	0.0695	0.0777	0.0777	0.46	0.44	0.45
Pt/Ce-ZrO$_2$	1	CH$_4$/CO$_2$ (2:1)/H$_2$O	0.1145	0.1145	0.1063	0.69	0.68	0.49
Pt/Ce-ZrO$_2$	8	CH$_4$/CO$_2$ (2:1)	0.7196	0.2290	–	0.51	0.49	–
Pt/Ce-ZrO$_2$	14	CH$_4$/CO$_2$ (2:1)	1.202	0.115	–	0.46	0.36	–

CH$_4$:CO$_2$ ratio (2:1). It can be seen that the conversions of CH$_4$ and CO$_2$ slightly decreased on the Pt/ZrO$_2$ catalysts. After 22 h of reaction, the H$_2$/CO ratio was around 0.42.

As it was observed for the reaction with a CH$_4$:CO$_2$ ratio of 1:1, the Pt/Ce-ZrO$_2$ catalyst was more active and did not deactivate during the 22 h (figure 2(b)), while the H$_2$/CO ratio was approximately the same (0.45).

These results are in agreement with previous studies of Stagg and Resasco [17] using a CH$_4$: CO$_2$ ratio of

2:1. They observed that Pt supported on Ce-promoted ZrO$_2$ containing around 5% Ce was much more stable than the unpromoted Pt/ZrO$_2$ catalyst. According to them, the higher stability of the promoted catalyst was due to the higher CO$_2$ adsorption capacity, which increased the dissociation and cleaning ability. Although it is known that the addition of Ce has an effect on surface area, the 5 wt% Ce-promoted support presented approximately the same surface area as that of the unpromoted support. Therefore, it was concluded that
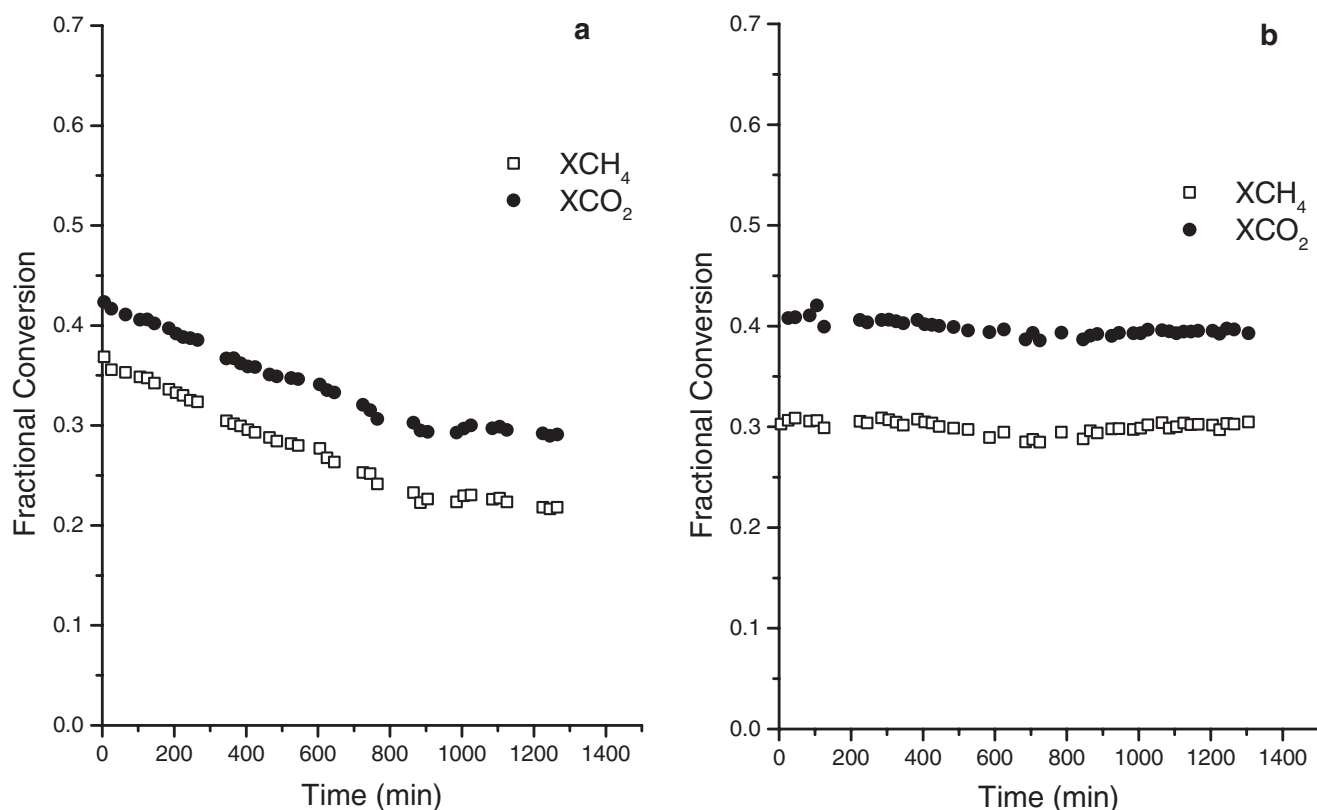

Figure 1. (□) CH$_4$ and (●) CO$_2$ conversions on the CO$_2$ reforming of methane in the absence of water ($T = 1073$ K; $p = 1$ atm; CH$_4$:CO$_2 = 1:1$) on (a) Pt/ZrO$_2$ and (b) Pt/Ce-ZrO$_2$.
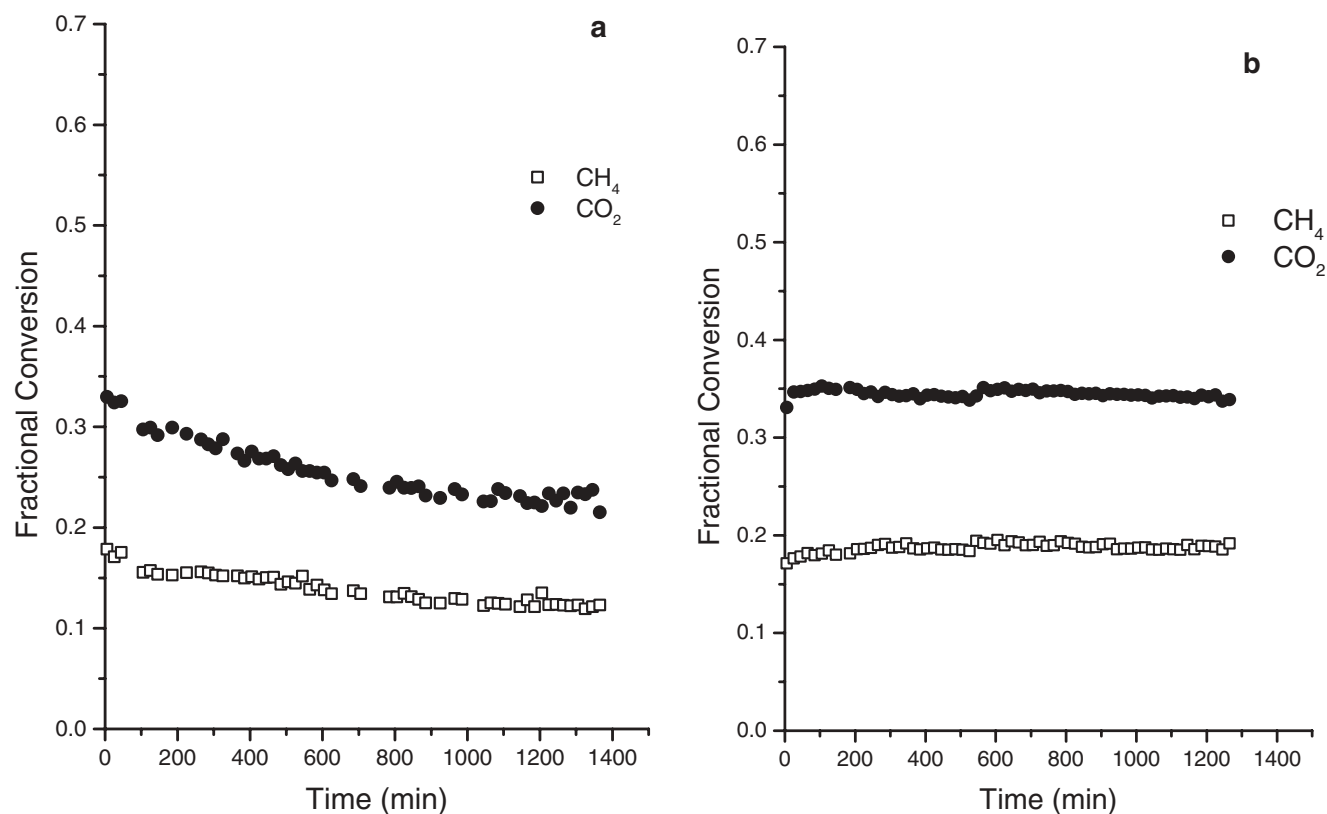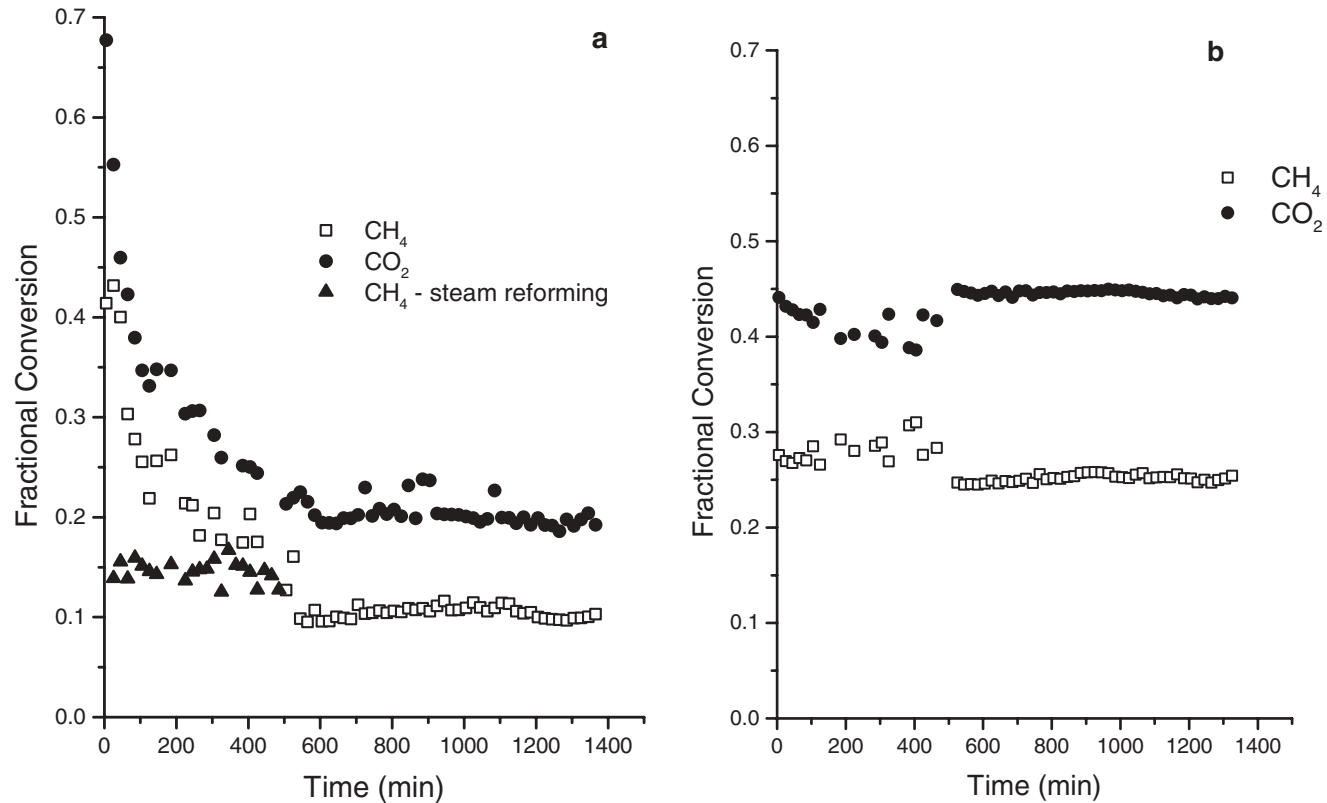
Figure 2. ($\square$) CH_4 and ($\bullet$) CO_2 conversions on the CO_2 reforming of methane in the absence of water ($T = 1073\,K$; $p = 1\,atm$; $CH_4:CO_2 = 2:1$) on (a) Pt/ZrO_2 and (b) $Pt/Ce-ZrO_2$.

Figure 3. ($\square$) CH_4 and ($\bullet$) CO_2 conversions on the CO_2 reforming of methane in the presence of water ($T = 1073\,K$; $p = 1\,atm$; $CH_4:CO_2 = 2:1$; $15\,mL/\min\,H_2O$) on (a) Pt/ZrO_2 and (b) $Pt/Ce-ZrO_2$. ($\blacktriangle$) CH_4 conversion on the steam reforming of methane on the Pt/ZrO_2 catalyst.

the most important effect of the incorporation of CeO$_2$ to ZrO$_2$ lattice is to increase the oxygen vacancies of the support due to a higher oxygen mobility [19]. Increasing the weight percent of Ce to 17.5% resulted in an increase in the surface area for the Ce-promoted support (48 m^2/g) compared to the unpromoted support (25 m^2/g). The XRD analysis indicated that the support maintained the tetragonal form of ZrO$_2$ with the addition of 17.5 wt% Ce, but formed the cubic structure at a Ce : Zr ratio of 1.0. At the same time, EXAFS analysis revealed that the addition of the Ce and La promoters decreased the metal particle growth under reaction conditions. Sintering not only would reduce the area of active metal but also decrease the metal–support interaction, limiting the removal of carbon from the metal.

An increase in the CH$_4$: CO$_2$ ratio had a negative effect on the activity of both promoted and unpromoted catalysts. Similar behavior has been observed by van Keulen *et al.* [8] on a 0.82% Pt/ZrO$_2$ catalyst when the CH$_4$: CO$_2$ ratio was increased from 0.5 to 1.0. The activity decrease is most probably due to a higher rate of carbon deposition that quickly reduces the catalyst activity, reaching a more stable activity at a lower rate.

3.2. Combined CO$_2$ reforming and steam reforming

In the presence of water, the initial conversions of CH$_4$ and CO$_2$ were high on the ZrO$_2$-supported catalyst (43% and 68% respectively) (figure 3(a)). However, the CO$_2$ conversion decreased quickly and continuously while water was present. The higher methane conversion is due to the reaction with steam, which also explains the higher H$_2$/CO ratio obtained (table 1). Moreover, it is possible that a fraction of excess H$_2$ reacts with more CO$_2$ through the reverse water-gas shift reaction as found by Hegarty *et al.* [20] on the Pt/ZrO$_2$ catalyst. The observed deactivation could be ascribed to the formation of carbon deposits on the metal, which decreases the methane decomposition. This suggests that the cleaning capacity of the support decreased in the presence of water. It appears that water plays a major role in the deactivation of the Pt/ZrO$_2$ catalyst under combined dry reforming and steam reforming. In fact, Otsuka *et al.* [21] have shown that water can reoxidize reduced cerium oxide. Then, the lower stability of the Pt/ZrO$_2$ catalyst could be explained by the oxidation of the partially reduced zirconium oxide species by the water, thus decreasing the density of oxygen vacancies on the support. The disappearance of these vacancies could inhibit the CO$_2$ dissociation and therefore the metal-cleaning rate.

Hegarty *et al.* [20] performed the CO$_2$ reforming of methane (CH$_4$: CO$_2$ ratio of 1 : 1; reaction temperature: 800 °C) on a Pt/ZrO$_2$ catalyst in the presence of different levels of water content. They observed that the addition of water increased the activity, which was attributed to the steam reforming reaction. But, they did not evaluate the catalytic behavior during long reaction times. According to our results, the Pt/ZrO$_2$ catalyst, which generally presents a good stability on the dry reforming, can suffer a strong deactivation in the presence of water.

Interestingly, when water was removed, the CH$_4$ and CO$_2$ conversions stayed approximately constant at the value left after the reaction with water (figure 3(a)). A more drastic reduction was observed on the H$_2$/CO ratio, which decreased from 0.82 to 0.45 after 22 h. The recovery of the catalyst stability after water removal gives further support to the mechanism described above.

The Pt/ZrO$_2$ catalyst was much more stable for the steam-reforming reaction in the absence of CO$_2$ than when CO$_2$ was present (figure 3(a)). It is possible that without the presence of CO$_2$, the reaction between methane and water only occurs on the metal particle, without the participation of the support [22]. Therefore, deactivation of the catalyst is not observed even when the oxidation of the support by the water takes place. However, the support participates in the reaction mechanism when CO$_2$ is present and consequently, the oxidation of the ZrO$_2$ leads to a decrease of the catalyst stability.

Figure 3(b) shows the results of exposing the Pt/Ce-ZrO$_2$ catalyst to water. The catalytic behavior of the promoted catalyst for the combined dry reforming was completely different from the one observed on the unpromoted catalyst. The promoted catalyst was significantly more stable. The higher stability of the Pt/Ce-ZrO$_2$ catalyst supports the mechanism previously proposed by Stagg and Resasco [17]. Since the Ce-ZrO$_2$ support has a higher amount of oxygen vacancies, the role of the water on the oxidation of partially reduced support is not as important. This could explain the higher stability of the Pt/Ce-ZrO$_2$ catalyst even in the presence of water.

3.3. CO$_2$ reforming of methane under pressure

The CH$_4$ and CO$_2$ conversions during the CO$_2$ reforming of methane under 105 psig are displayed in figure 4. On both catalysts, the activity decreased during the reaction. Both CH$_4$ and CO$_2$ conversions dropped, but that of CO$_2$ decreased more markedly. Figure 5 shows the results of the CO$_2$ reforming of methane under $p = 190$ psig on the Pt/ZrO$_2$ and Pt/Ce-ZrO$_2$ catalysts. Although at 190 psig, both catalysts deactivate, the deactivation is more rapid on the unpromoted Pt/ZrO$_2$ catalyst than on the Ce-containing catalyst. The increase of pressure to 190 psig produced a higher deactivation of both catalysts, which correlates with a more thermodynamically favored carbon deposition [23].
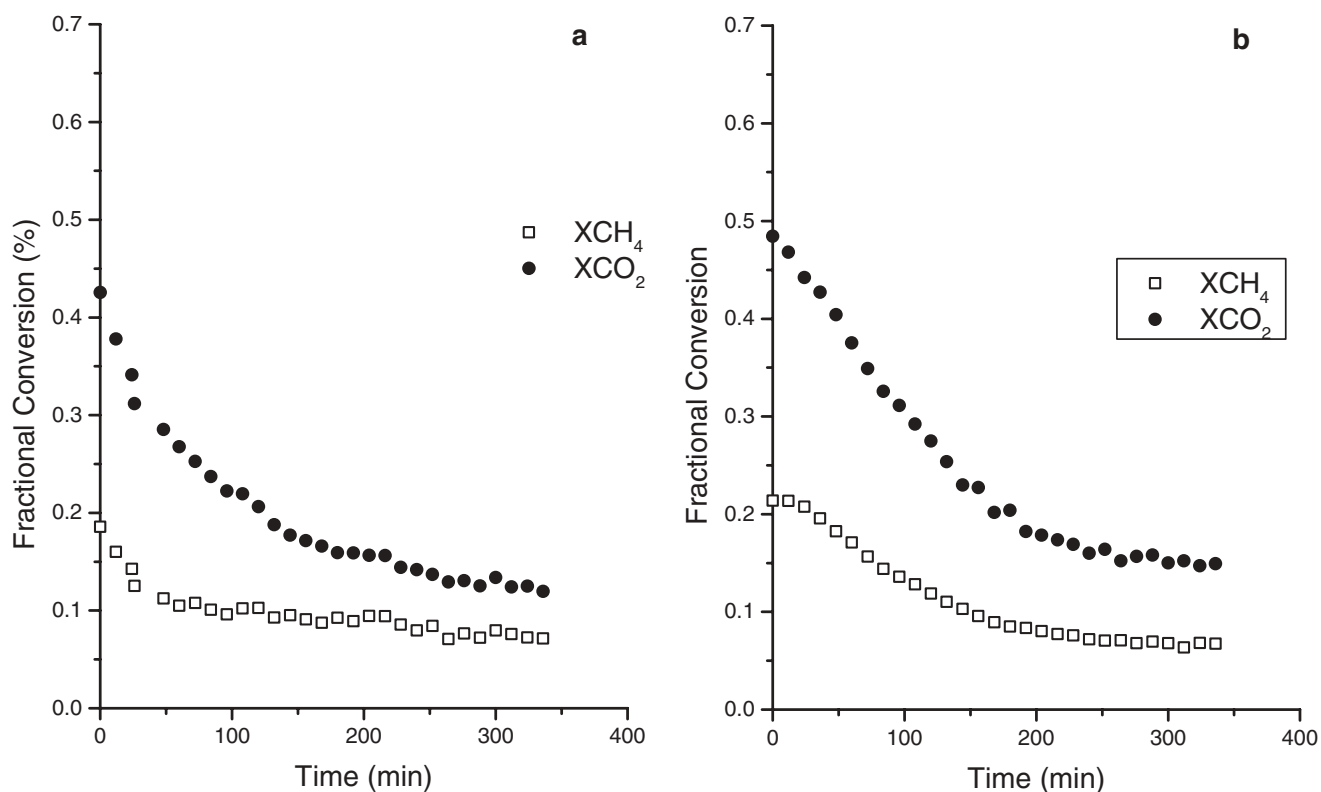
Figure 4. (□) CH_4 and (●) CO_2 conversions on the CO_2 reforming of methane under pressure ($T = 1073$ K; $p = 8$ atm; CH_4:$CO_2 = 2$:1) on (a) Pt/ZrO₂ and (b) Pt/Ce-ZrO₂.
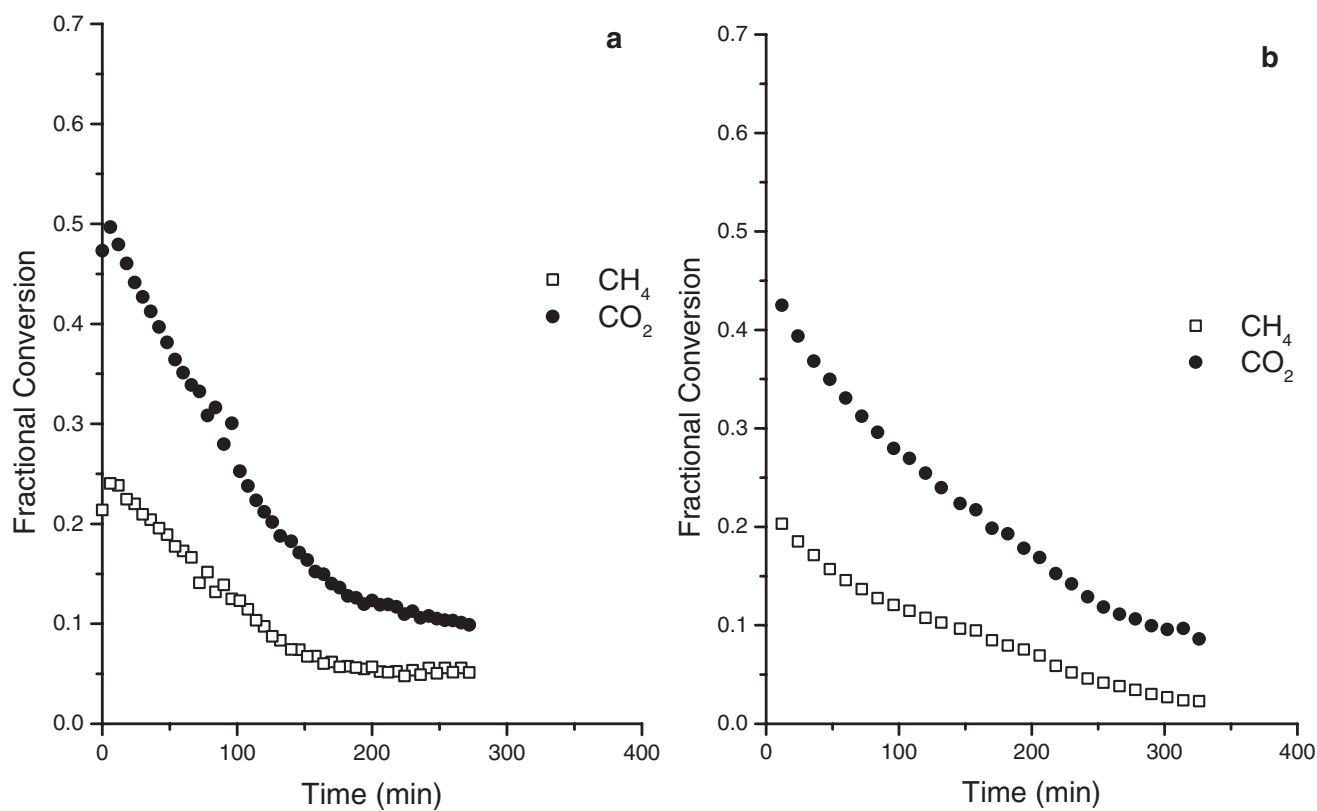
Figure 5. (□) CH_4 and (●) CO_2 conversions on the CO_2 reforming of methane under pressure ($T = 1073$ K; $p = 14$ atm; CH_4:$CO_2 = 2$:1) on (a) Pt/ZrO₂ and (b) Pt/Ce-ZrO₂.

3.4. TPO analysis

The TPO profiles of the Pt/ZrO$_2$ and Pt/Ce-ZrO$_2$ catalysts and the amount of coke formed after different reaction conditions are presented in figures 6 and 7 and table 2.

The CO$_2$ curves obtained during TPO of the Pt/ZrO$_2$ catalyst after dry reforming (CH$_4$: CO$_2$ = 1 : 1) exhibited a small, broad peak at 746 K and a large one at 964 K (figure 6(a)). The TPO profile of the Pt/Ce-ZrO$_2$ catalyst was similar to the one of the Pt/ZrO$_2$ catalyst, presenting two peaks at 738 and 967 K (figure 6(b)). The amount of carbon formed on the Pt/ZrO$_2$ catalyst was significantly higher than on the Pt/Ce-ZrO$_2$ catalyst.

Recently, we studied the stability of the Pt/ZrO$_2$, Pt/CeO$_2$ and Pt/Ce-ZrO$_2$ catalysts on the CO$_2$ reforming of methane and its relationship with the nature and location of carbon deposits [19].

TPO measurements revealed that there is no correlation between the amount of carbon deposited and stability. TPO profiles of all catalysts exhibited two peaks in the low-temperature region (623–723 K) and high-temperature region (873–973 K). The first was more important in the unpromoted catalysts, whereas the second one was dominant in the Pt/Ce-ZrO$_2$ catalysts. XPS and TPO analysis showed that the
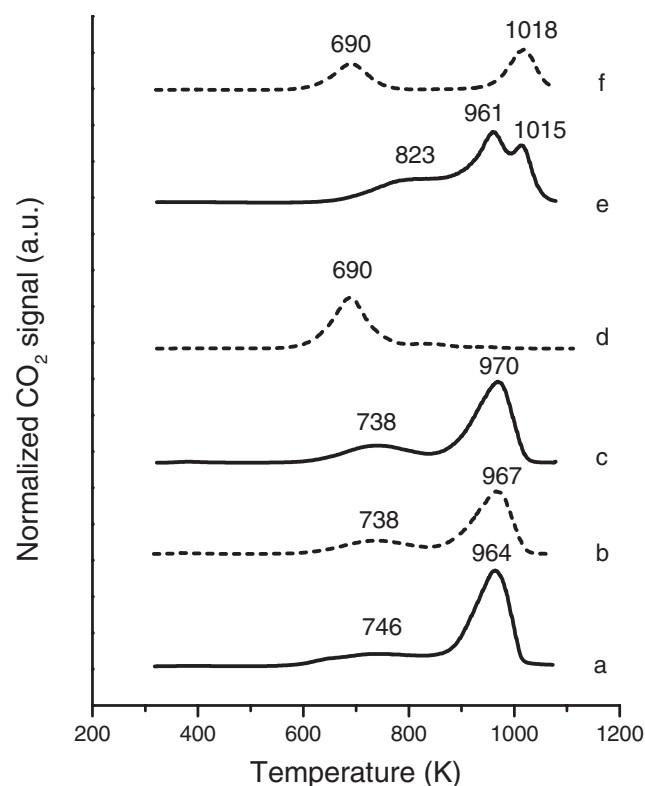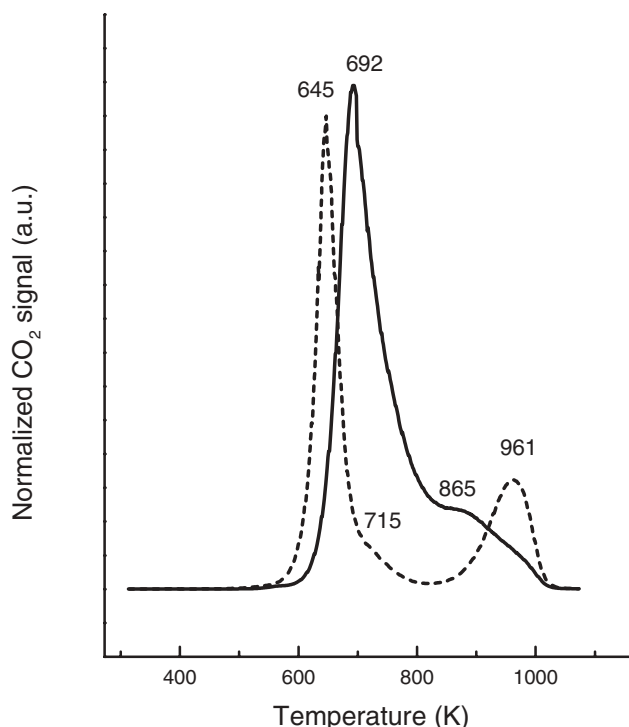

Figure 7. CO$_2$ signal during TPO analysis after CO$_2$ reforming of methane under 14 atm (100 mg of catalyst) on (a) Pt/ZrO$_2$ and (b) Pt/Ce-ZrO$_2$.

different peaks observed in TPO profile are due to carbon in different locations on the catalyst surface. On the Pt/Ce-ZrO$_2$ catalyst, the low-temperature TPO peak was ascribed to carbon near the metal particle since this catalyst did not deactivate. The high-temperature peak was attributed to carbon on the support.

The CO$_2$ signal during oxidation on the Pt/ZrO$_2$ catalyst after dry reforming (CH$_4$: CO$_2$ = 2 : 1) (figure 6(c)) was very similar to the one obtained under CH$_4$: CO$_2$ ratio of 1 : 1. On the Pt/Ce-ZrO$_2$ catalyst, the CO$_2$ signal during TPO showed just one peak at low temperature (688 K) (figure 6(d)). Under these reaction conditions, the amount of carbon deposited on both catalysts was higher than under a CH$_4$: CO$_2$ ratio of 1 : 1 and was in agreement with the lower activity observed of these catalysts. The lower activity of the catalysts in the presence of CH$_4$: CO$_2$ = 2 : 1 can be explained by the two-path mechanism proposed [17–19]. This mechanism is based on the balance resulting from the methane decomposition and the oxygen transfer rate. When the CH$_4$: CO$_2$ ratio is increased to 2 : 1, the rate of methane decomposition is faster than the oxygen transfer and carbon deposition occurs until a balance is achieved. Under the CH$_4$: CO$_2$ ratio of 1 : 1, the balance is obtained faster since the methane concentration on the metal surface is lower and the activity stabilizes at a high rate.

After CO$_2$ reforming in the presence of water, the CO$_2$ curve of the Pt/ZrO$_2$ catalyst displayed two peaks at 804 and 960 K and a new one at high temperature

Figure 6. CO$_2$ signal during TPO analysis after: CO$_2$ reforming of methane with CH$_4$: CO$_2$ = 1 : 1 on (a) Pt/ZrO$_2$, (b) Pt/Ce-ZrO$_2$, CO$_2$ reforming of methane with CH$_4$: CO$_2$ = 2 : 1 on (c) Pt/ZrO$_2$, (d) Pt/Ce-ZrO$_2$, CO$_2$ reforming of methane with CH$_4$: CO$_2$ = 2 : 1 in the presence of water, (e) Pt/ZrO$_2$ and (f) Pt/Ce-ZrO$_2$.

Table 2
TPO results of the amount of coke formed after different reaction conditions on Pt/ZrO$_2$ and Pt/Ce-ZrO$_2$ catalysts

Catalyst	Total pressure (atm)	Feed	Amount of carbon (gmol C/g$_{cat}$) $\times 10^{-3}$	C/Pt ratio
Pt/ZrO$_2$	1	CH$_4$/CO$_2$ (1:1)	1.08	14.0
Pt/ZrO$_2$	1	CH$_4$/CO$_2$	1.60	20.8
Pt/ZrO$_2$	1	CH$_4$/CO$_2$/H$_2$O	2.60	33.8
Pt/ZrO$_2$	1	CH$_4$/H$_2$O	2.76	35.9
Pt/ZrO$_2$	14	CH$_4$/CO$_2$	7.27	94.5
Pt/Ce-ZrO$_2$	1	CH$_4$/CO$_2$ (1:1)	0.61	7.91
Pt/Ce-ZrO$_2$	1	CH$_4$/CO$_2$	2.09	27.2
Pt/Ce-ZrO$_2$	1	CH$_4$/CO$_2$/H$_2$O	2.90	37.7
Pt/Ce-ZrO$_2$	14	CH$_4$/CO$_2$	5.55	72.2

(1012 K) (figure 6(e)). The same behavior was observed on the Pt/Ce-ZrO$_2$ catalyst with the appearance of a peak at 1019 K (figure 6(f)). Moreover, the addition of water to CO$_2$ reforming of methane increased the amount of deposited coke (table 2). These results support the proposal that water reduces the amount of vacancies on the support, inhibiting its cleaning capacity, which results in a higher accumulation of carbon.

The CO$_2$ profiles during TPO after reaction under 190 psig (100 mg catalyst : 22 h of reaction) are displayed on figure 7. The CO$_2$ curve of the Pt/ZrO$_2$ catalyst exhibited a wide peak at 692 K and a shoulder around 865 K. On the Pt/Ce-ZrO$_2$ catalyst, the CO$_2$ signal showed two peaks, one at 645 K and another at 961 K. The amount of carbon deposited on both catalysts strongly increased. Furthermore, it is noted that the intensity of the low-temperature peak strongly increased. This result indicates that under high pressure, the rate of oxygen transfer is not enough to keep the proximity of the metal–support interface free of coke and the catalyst deactivates.

4. Conclusions

The Pt/Ce-ZrO$_2$ catalyst was very stable on the CO$_2$ reforming of methane using CH$_4$:CO$_2$ ratio of 1:1 or 2:1. The increase of the CH$_4$:CO$_2$ ratio decreased the activity of Pt/ZrO$_2$ and Pt/Ce-ZrO$_2$ catalyst owing to the higher carbon deposition as demonstrated by TPO analysis. In agreement with the two-step mechanism, at higher CH$_4$:CO$_2$ ratios, the rate of methane decomposition is faster than the oxygen transfer, and carbon deposition occurs until a balance is achieved.

The CO$_2$ reforming of methane in the presence of water proceeded differently on both catalysts. The addition of water strongly decreased the CH$_4$ and CO$_2$ conversion during the reaction on the Pt/ZrO$_2$ catalysts. TPO analysis showed that the addition of water increased the amount of deposited carbon. The lower stability of the Pt/ZrO$_2$ catalyst was due to the

oxidation and decrease of the amount of oxygen vacancies by the water, inhibiting the cleaning mechanism. On the other hand, Pt/Ce-ZrO$_2$ catalyst was quite stable in the presence of water. This stability was ascribed to the higher amount of oxygen vacancies of the support. Both catalysts were relatively stable on the CO$_2$ reforming of methane under 105 psig, however, both catalysts deactivated quickly under high pressure (190 psig). TPO analysis revealed that the amount of carbon deposited on both catalysts strongly increased.

Acknowledgments

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